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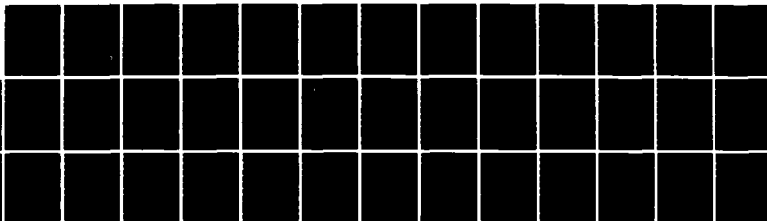
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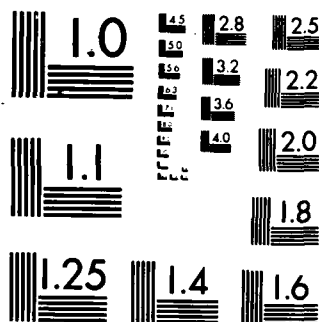
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Infrared-Laser Excitation of the Internal Vibrational Mode of a  
Diatomic Molecule Adsorbed on a Metal Surface

by

André Peremans, Jacques Darville, Jean-Marie Gilles and Thomas F. George

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State University of New York at Buffalo  
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INFRARED-LASER EXCITATION OF THE INTERNAL VIBRATIONAL MODE  
OF A DIATOMIC MOLECULE ADSORBED ON A METAL SURFACE

André Peremans<sup>†</sup>, Jacques Darville and Jean-Marie Gilles  
Laboratoire de Spectroscopie Moléculaire de Surface  
Département de Physique  
Facultés Universitaires Notre-Dame de la Paix  
61, rue de Bruxelles  
B-5000 Namur, BELGIUM

and

Thomas F. George  
Departments of Chemistry and Physics & Astronomy  
State University of New York at Buffalo  
Buffalo, New York 14260 USA

Abstract

The infrared-laser excitation of the internal vibrational mode of a diatomic molecule adsorbed on a metal surface is analyzed theoretically. This vibrational energy is damped into the metal by electron-hole excitations. Simple expressions for the populations of the vibrational levels, the mean number of vibrational quanta and the rate of energy transfer between the infrared laser and the metal surface at the steady state are derived. An equation of evolution can readily be solved numerically to determine the time necessary to reach this steady state. The criteria of applicability of the Markov approximation (which leads to the golden rule) is clearly established, where it is seen that this approximation may not be used to compute the evolution of the populations of the vibrational levels. The random-phase approximation is shown to give the correct kinetic equation for the populations of the vibrational levels. The excitation of carbon monoxide adsorbed on a copper surface is analyzed quantitatively.

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<sup>†</sup> Aspirant du Fonds National de la Recherche Scientifique, Bruxelles

## I. Introduction

The excitation of a molecular vibration can significantly contribute to overcoming the activation barrier of a chemical reaction. This fact has led to many attempts to modify the course of surface processes by resonant excitation of vibrational modes by means of infrared laser radiation [1]. Due to their importance in catalysis, laser-stimulated reactions at metal surfaces have been investigated [2-6]. For example, it has been shown that focused infrared laser radiation can induce resonant ionization of adspecies [2] or gaseous species above a surface [3], where the fragments from the latter process can then undergo surface reactions which are not possible with the original molecules. Even when the laser is not focused, the resonant excitation of a gaseous species can decrease the likelihood of physisorption [4] or increase the tendency for dissociative chemisorption [5]. When laser radiation impinges on a gas-solid interface, it can excite the substrate, adsorbate and/or species in the gas phase. Chuang [7] has demonstrated that resonant excitation of the adsorbate can stimulate etching of a silicon surface by  $\text{SF}_6$ . While this mechanism of adsorbate resonant excitation has been proposed for experiments involving metal surfaces [6], it is perhaps not as obvious here since the vibrational energy of a metal adsorbate quickly damps into the metal, as observed by infrared reflection absorption spectroscopy [8,9]. This leads to two questions: (1) Can an infrared laser beam maintain a high surface concentration of vibrationally-excited molecules, and (2) what is the rate of energy transfer from the laser to the metal through the adsorbed molecules? Such energy transfer leads to resonant heating of the substrate, which can then "thermally" enhance a surface reaction or the desorption of the adsorbate before reaction occurs. These questions have motivated us to carry out a

theoretical study of the simple case of the resonant interaction of infrared laser radiation with a diatomic molecule adsorbed on a metal surface.

The spectral infrared absorption width of a diatomic molecule in the gas phase is of the order of  $10^{-2} \text{ cm}^{-1}$ . When the molecule is adsorbed on a metal, this width may reach many  $\text{cm}^{-1}$  [8]. This broadening was successfully explained by Persson in terms of electron transfer between the adsorbate and the substrate [10], and this mechanism has been confirmed by means of cluster calculations [11]. The lifetime of an excited vibrational state was estimated to be of the order of  $10^{-12} \text{ s}$ . This is much shorter than the lifetime due to other mechanisms such as phonon-phonon energy transfer ( $\sim 10^{-9} \text{ s}$ ) [12-17] or dipole-hole-electron interactions ( $\sim 10^{-10} \text{ s}$ ) [18]. We shall thus assume electron transfer to be the only mechanism responsible for energy transfer between the substrate and the adsorbate.

Theoretical studies already presented in the literature related to the interaction of an infrared laser beam with adsorbed molecules are focused on the phonon-phonon energy transfer between the substrate and the adsorbate. The computational techniques used are the "golden rule" [13,14] and the transformation to dressed states [15-17]. The Zwanzig projector technique [19] within the Born, the random-phase and the Markov approximations has been used to compute molecular desorption rates [12]. We shall use the Zwanzig projector technique within the Born approximation only, and shall obtain simple expressions describing the kinetic and the steady state of our system. Furthermore, our results will provide criteria for the applicability of all the approximations listed above.

In Section II we present our model and write down the Hamiltonian. In Section III we derive the kinetic equation for the density operator characterizing the vibrational state of the adsorbed molecule. In Section

IV we analyze the memory kernels, where the validity of the Markov approximation is questioned. In Section V we derive the properties of the steady state and the equation of evolution of the populations of the vibrational levels, where we look at the effect of anharmonicity by restricting our equations to a two-level system. In Section VI we present some numerical results, and we end with the conclusions in Section VII.

## II. Model

The internal vibrational mode of the adsorbed diatomic molecule is assumed to be harmonic, with the molecule adsorbed perpendicular to the surface. The infrared laser beam is collimated and polarized in such a way that the electric field is parallel to the axis of symmetry of the molecule. This simplification is valid because an infrared beam can only create an electric field perpendicular to the surface in its vicinity [20]. The laser is tuned in resonance with the internal molecular vibration. The adsorbate-substrate electronic system is taken to be in the ground state, so that the vibration of the adsorbed molecule creates electron-hole pairs. This causes a strong damping of the vibrational energy into the metal. This approximation is valid if  $\hbar\omega \gg kT$ , where  $T$  is the temperature of the metal,  $k$  is the Boltzmann constant, and  $\omega$  is the frequency of vibration of the molecule.

The Hamiltonian can be written in the second-quantization form as

$$\begin{aligned}
 H = & \sum_S \epsilon_S E_S^\dagger E_S + \sum_S [V_{aS} E_S^\dagger a + \text{h.c.}] + \epsilon_a a^\dagger a + V_a(\xi) a^\dagger a + \sum_b \epsilon_b b^\dagger b \\
 & + \sum_b V_b(\xi) b^\dagger b + H^{rv} + H^r + KE \quad .
 \end{aligned} \tag{1}$$



Here  $E_S^\dagger$  is the creation operator of one electron in the state  $|S\rangle$  of the unperturbed metal;  $a^\dagger$  and  $b^\dagger$  are creation operators of electrons in the orbitals  $|a\rangle$  and  $|b\rangle$ , respectively, of the free diatomic molecule;  $\xi$  is the coordinate associated with the stretching of the molecule; and  $KE$  is the kinetic energy associated with  $\xi$ .  $|a\rangle$  is assumed to be the only molecular orbital interacting with the electronic orbitals  $|S\rangle$  of the metal, and this interaction gives the factor  $V_{aS}$ .  $\epsilon_a + V_a(\xi)$ ,  $\epsilon_b + V_b(\xi)$  and  $\epsilon_S$  are the Hartree-Fock energies of the electrons in the orbitals  $|a\rangle$ ,  $|b\rangle$  and  $|S\rangle$ , respectively.  $H^r$  is the Hamiltonian of the radiation, given by

$$H^r = \sum_k \hbar \omega_k \left( p_k^\dagger p_k + \frac{1}{2} \right) . \quad (2)$$

Here  $k$  is the norm of the wave vector,  $\vec{k}$ , of the photons, where  $\vec{k}$  is parallel to the direction of propagation of the beam,  $\vec{k} = k\hat{k}_0$ , and  $p_k^\dagger$  is the creation operator of one photon of wave vector  $k\hat{k}_0$ . The light is contained within a cubic quantization volume  $U$ .  $H^{rv}$  is the interaction Hamiltonian between the molecule and the infrared beam. Since we are only concerned with the coupling between the molecular stretching and the electronic system, we have neglected the dependence of this Hamiltonian on the positions of the metal nuclei and molecule with respect to the surface. We have also assumed a weak dependence of  $V_{aS}$  on versus  $\xi$ . This is a generalization of the Hamiltonian written by Persson [10].

We can decompose  $H$  as

$$H = H^e + H^v + H^r + H^{ev} + H^{rv} , \quad (3)$$

where  $H^e$  is the electronic Hamiltonian,

$$H^e = \sum_S \epsilon_S E_S^\dagger E_S + \sum_S [V_{aS} E_S^\dagger a + \text{h.c.}] + \epsilon_a a^\dagger a + \sum_b \epsilon_b b^\dagger b , \quad (4)$$

and can be formally diagonalized to give

$$H^e = \sum_{\beta} \epsilon_{\beta} C_{\beta}^{\dagger} C_{\beta} + \sum_{\beta} \epsilon_b b^{\dagger} b \quad (5)$$

where

$$a = \sum_{\beta} \langle a | \beta \rangle C_{\beta} \quad (6)$$

The vibrational Hamiltonian is given by

$$H^v = \langle g | V_a(\xi) a^{\dagger} a + \sum_b V_b(\xi) b^{\dagger} b | g \rangle + KE \quad (7)$$

where  $|g\rangle$  is the ground state of the electronic system.  $H^v$  is assumed to be the Hamiltonian of an harmonic oscillator,

$$H^v = \frac{\mu\omega^2\xi^2}{2} + \frac{\mu\dot{\xi}^2}{2} = \hbar\omega[V^{\dagger}V + \frac{1}{2}] \quad (8)$$

where  $\mu$  is the reduced mass of the molecule and  $V^{\dagger}$  is the creation operator for a vibrational quantum.  $H^{rv}$  is then given by

$$H^{rv} = \delta\xi E = \delta\left(\left(\frac{\hbar}{2\mu\omega}\right)^{1/2}[V^{\dagger} + V]\right)\left(-i\left(\frac{\hbar}{2\epsilon_0 U}\right)^{1/2} \sum_k \omega_k [p_k^{\dagger} - p_k]\right) \quad (9)$$

where  $\delta$  is the effective charge carried by the stretching coordinate  $\xi$ ,  $E$  is the electric field, and  $\epsilon_0$  is the dielectric constant of the vacuum.  $H^{ev}$  is given by

$$H^{ev} = V_a(\xi) a^{\dagger} a + \sum_b V_b(\xi) b^{\dagger} b - \langle g | V_a(\xi) a^{\dagger} a + \sum_b V_b(\xi) b^{\dagger} b | g \rangle \quad (10)$$

We approximate  $V_a(\xi)$  by

$$V_a(\xi) \approx \frac{\partial \epsilon_a}{\partial \xi} \xi = \frac{\partial \epsilon_a}{\partial \xi} \left(\frac{\hbar}{2\mu\omega}\right)^{1/2} (V^{\dagger} + V) \quad (11)$$

### III. Kinetic Equation

To compute the evolution of the vibrational state of the molecule, we shall use the Zwanzig projector technique [19]. In this approach, Zwanzig derived an exact kinetic equation for the density operator of one subsystem interacting with another one, which will be named bath subsystem. In our situation the first subsystem will be the internal vibrational mode of the adsorbed diatomic molecule. It interacts with the bath subsystem, which is constituted by two independent subsystems: the laser beam and the electronic system. The interaction Hamiltonian between the vibration and the bath is given by

$$H^I = \left(\frac{\hbar}{2\mu\omega}\right)^{1/2} (V^\dagger + V) B, \quad (12)$$

where

$$B = B^e \otimes I_r + B^r \otimes I_e. \quad (13)$$

Here  $I_r$  and  $I_e$  are, respectively, the identity operator of the radiative and electronic subsystem,  $\otimes$  symbolizes the outer product, and

$$B^e = \frac{\partial \epsilon_a}{\partial \xi} (a^\dagger a + \langle g | a^\dagger a | g \rangle) \quad (14)$$

$$B^r = -i\delta\left(\frac{\hbar}{2\epsilon_0 U}\right)^{1/2} \sum_k \omega_k [p_k^\dagger - p_k]. \quad (15)$$

We have removed the dependence of  $H^{ev}$  on the electronic degrees of freedom corresponding to the occupation of the molecular orbitals  $|b\rangle$ . This simplification comes from the fact that these orbitals are not coupled with the electronic orbitals  $|S\rangle$  of the metal, which can be verified by computing

explicitly the memory kernels in Eq. (24) or (28) below, where no specification on the form of  $H^I$  is needed.

The starting operator of the complete system  $[\rho(t = 0)]$  is taken to be the outer product of the vibrational  $[\rho^V(t = 0)]$  and the bath ( $\rho^b$ ) density operator,

$$\rho(0) = \rho^V(0) \otimes \rho^b. \quad (16)$$

We assume the vibrational subsystem to be in its ground state at time  $t = 0$ ,

$$\rho^V(0) = |0\rangle\langle 0|. \quad (17)$$

The density operator of the bath subsystem is itself the outer product of the radiative ( $\rho^r$ ) and electronic ( $\rho^e$ ) subsystem:

$$\rho^b = \rho^e \otimes \rho^r. \quad (18)$$

The electronic subsystem is taken to remain in its ground state,

$$\rho^e = |g\rangle\langle g|. \quad (19)$$

The density operator of the radiative subsystem corresponds to a statistical superposition of coherent states with different phase [21].  $\rho^r$  is then diagonal in the radiative Hamiltonian eigenstate representation,

$$\rho^r = \sum_{kn} p_{kn} |kn\rangle\langle nk|. \quad (20)$$

We note that  $\rho^V(0)$ ,  $\rho^b$ ,  $H^V$  and  $H^b$  ( $= H^e + H^r$ ) commute with each other.

Furthermore,

$$\text{Tr}_{\text{er}}\{H^I \cdot \rho^b\} = \bar{0}, \quad (21)$$

where  $\text{Tr}_{\text{er}}\{ \}$  is the trace over all the electronic and radiative states.

To obtain a tractable kinetic equation, we shall invoke the Born approximation [12]. This approximation is valid if the interaction Hamiltonian between the vibrational and bath systems is small in comparison with the Hamiltonians driving their evolutions independently ( $H^V \gg H^I \ll H^b$ ). It then follows from that the kinetic equation can be written as [12]

$$\begin{aligned} i\hbar \dot{\rho}^V(t) = [H^V, \rho^V(t)] - \frac{i}{\hbar} \int_0^t ds \quad (22) \\ \times \text{Tr}_{\text{er}}\{[H^I, \exp(-iH^V s/\hbar)[H^I(-s), \rho^V(t-s) \otimes \rho^b] \exp(iH^V s/\hbar)]\} \quad , \end{aligned}$$

where the density operator of the vibrational system is defined by  $\rho_V(t) = \text{Tr}_{\text{er}}\{\rho(t)\}$ , and

$$H^I(-s) = \exp(-iH^b s/\hbar) H^I \exp(iH^b s/\hbar). \quad (23)$$

Equation (23) can be written in terms of the matrix element  $\rho_{mn}^V(t)$  ( $= \langle m | \rho^V(t) | n \rangle$ ) simply by multiplying it respectively on the left and by the right with  $\langle m |$  and  $| n \rangle$ . The derivation in the case where  $m = n$  is given in Ref. 12. The generalization to the case  $m \neq n$  is straightforward. We observe that the integrand in (22) contains a double commutator, corresponding to four terms. To simplify the notation, we shall track explicitly just one of these terms, keeping in mind that the others must be treated in the same way. We then arrive at

$$\begin{aligned} \dot{\rho}_{nm}^V(t) = -i\omega_{nm} \rho_{nm}^V(t) - \frac{1}{\hbar^2} \int_0^t ds \{ 3 \text{ terms} - \int_{\text{op}} \exp(i\omega_{pn} s) \\ \times \langle H_{pm}^I H_{no}^I(-s) \rangle \rho_{op}^V(t-s) \} \quad , \quad (24) \end{aligned}$$

where

$$H_{pm}^I = \langle p | H^I | m \rangle ,$$

$$\langle K \rangle = \text{Tr}_{er} \{ K \cdot \rho^b \},$$

and

$$\omega_{nm} = (E_n^V - E_m^V)/\hbar = (n - m)\omega .$$

To solve these coupled equations, we transform into the interaction picture by defining

$$\rho_{nm}^V(t) = \tilde{\rho}_{nm}^V(t) \exp(-i\omega_{nm}t) . \quad (25)$$

After some simple algebra, we end up with

$$\begin{aligned} \dot{\rho}_{nm}^V(t) = & -\frac{1}{\hbar^2} \left\{ 3 \text{ terms} - \int_{op} \exp[i(\omega_{po} + \omega_{nm})t] \int_0^t ds \exp(i\omega_{on}s) \right. \\ & \times \langle H_{pm}^I H_{no}^I(-s) \rangle \tilde{\rho}_{op}^V(t-s) \} . \end{aligned} \quad (26)$$

Without any interaction ( $H^I = \bar{0}$ ), the quantities  $\tilde{\rho}_{op}^V(t-s)$  are constant. With  $H^I \neq \bar{0}$ , they are expected to vary only on a time scale much greater than the oscillation period of the vibration. Thus the only terms in the sum " $\int_{op}$ " which give rise to a variation of  $\tilde{\rho}_{nm}^V(t)$  during a period corresponding to several oscillations are the ones verifying

$$\omega_{po} + \omega_{nm} = 0 \quad \text{or} \quad p = m - n + o . \quad (27)$$

Neglecting all the others, we can write the following kinetic equation where

we use  $\langle H_{ij}^I(-s) H_{kl}^I \rangle = \langle H_{kl}^I H_{ij}^I(-s) \rangle^*$ ,  $\tilde{\rho}_{ij}^V = \tilde{\rho}_{ji}^{V*}$ ,  $H_{kl}^I = H_{lk}^I$ :

$$\dot{\rho}_{nm}^V(t) = -\frac{1}{\hbar^2} \int_0^t ds$$

$$\begin{aligned}
& \times \int_0^{\infty} \{ \exp(i\omega_{no}s) \langle H_{no}^I H_{on}^I(-s) \rangle \tilde{\rho}_{nm}^v(t-s) \\
& + [ \exp(i\omega_{mo}s) \langle H_{mo}^I H_{om}^I(-s) \rangle \tilde{\rho}_{nm}^v(t-s)]^* \} \\
& - \int_0^{\infty} \{ \exp(i\omega_{on}s) \langle H_{(m-n)+o,m}^I H_{no}^I(-s) \rangle \tilde{\rho}_{o,(m-n)+o}^v(t-s) \\
& + [ \exp(i\omega_{om}s) \langle H_{(n-m)+o,n}^I H_{m,o}^I(-s) \rangle \tilde{\rho}_{o,(n-m)+o}^v(t-s)]^* \} . \quad (28)
\end{aligned}$$

The above equation gives us the following result: only the elements of the vibrational density matrix which belong to the same diagonal ( $\tilde{\rho}_{ij}$  with  $|j - i| = \text{constant}$ ) are coupled in the kinetic equation. More generally, even for an highly anharmonic vibration it is easy to see that the diagonal elements of  $\rho^v(t)$  evolve independently from the others [put  $m = n$  in Eqs. (26), (27) and (28)]. The importance of this result will be emphasized in Section VII. In our situation, further simplifications can be made. Using (12) we find that  $\langle H_{(m-n)+o,m}^I H_{no}^I(-s) \rangle$  is different from zero only if  $o = n \pm 1$ . In the case where  $o = n + 1$ , it is equal to  $\frac{\hbar}{2\mu\omega} [(m+1)(n+1)]^{1/2} \times D(-s)$ , where  $D(-s)$  is defined as

$$D(-s) \equiv \langle B B(-s) \rangle . \quad (29)$$

The kinetic equation can then be written as

$$\begin{aligned}
\dot{\tilde{\rho}}_{nm}^v(t) = & - \frac{1}{2\hbar\mu\omega} \int_0^t ds \{ ((n+1) \exp(-i\omega s) D(-s) \tilde{\rho}_{nm}^v(t-s) \\
& + n \exp(i\omega s) D(-s) \tilde{\rho}_{nm}^v(t-s)) \\
& + (m+1) [\exp(-i\omega s) D(-s) \tilde{\rho}_{nm}^v(t-s)]^* \\
& + m [\exp(i\omega s) D(-s) \tilde{\rho}_{nm}^v(t-s)]^* \}
\end{aligned}$$

$$\begin{aligned}
& - \{ [ (n+1)(m+1) ]^{1/2} \exp(i\omega s) D(-s) + \text{c.c.} \} \bar{\rho}_{n+1,m+1}^v(t-s) \\
& - \{ (\sqrt{mn} \exp(-i\omega s) D(-s) + \text{c.c.} \} \bar{\rho}_{n-1,m-1}^v(t-s) . \quad (30)
\end{aligned}$$

The kinetic equation for the diagonal elements is

$$\begin{aligned}
\dot{P}_n(t) = & - \frac{1}{\hbar\mu\omega} \text{Re} \int_0^t ds \{ (n+1) \exp(-i\omega s) + n \exp(i\omega s) \} D(-s) P_n(t-s) \\
& - (n+1) \exp(i\omega s) D(-s) P_{n+1}(t-s) \\
& - n \exp(-i\omega s) D(-s) P_{n-1}(t-s) , \quad (31)
\end{aligned}$$

where  $P_n(t) = \bar{\rho}_{nn}^v(t) = \rho_{nn}^v(t)$ . A last simplification comes from the fact that

$$\langle B^e \rangle_e = \langle B^r \rangle_r = \bar{0} , \quad (32)$$

where  $\langle K \rangle_e = \text{Tr}_e \{ K \cdot \rho^e \}$ , and  $\text{Tr}_e \{ \}$  is the trace over all the electronic states (with a similar definition for  $\langle \rangle_r$ ).

The memory kernel then splits into two parts, one related to the interaction between the molecule and the laser, the other related to the interaction between the molecule and the substrate [22],

$$D(-s) = D^e(-s) + D^r(-s) , \quad (33)$$

where  $D^e(-s) = \langle B^e B^e(-s) \rangle_e$ , with a similar definition for  $D^r(-s)$ .

Because at time  $t = 0$  the nondiagonal elements of the vibrational density matrix are equal to zero, they will remain zero at all times. We are not interested in their evolution anyway, because the mean vibrational energy does not depend on them.



#### IV. Computation of the Memory Kernel

Let us first compute the part of the memory kernel due to  $H^{ev}$ . From (13), (23) and (33), we obtain

$$D^e(-s) = \left(\frac{\partial \epsilon_a}{\partial \xi}\right)^2 \langle g | (a^\dagger a - \langle g | a^\dagger a | g \rangle) \exp(-iH^e s / \hbar) \\ \times (a^\dagger a - \langle g | a^\dagger a | g \rangle) \exp(iH^e s / \hbar) | g \rangle . \quad (34)$$

Using (6) and its Hermitian conjugate, we can transform this into

$$D^e(-s) = \left(\frac{\partial \epsilon_a}{\partial \xi}\right)^2 \sum_{\epsilon_\alpha < \epsilon_f} \sum_{\epsilon_\beta > \epsilon_f} |\langle a | \alpha \rangle|^2 |\langle a | \beta \rangle|^2 \exp[-(\epsilon_\alpha - \epsilon_\beta)s / \hbar] . \quad (35)$$

This formula has been derived previously by Persson [10]. The new feature which we shall introduce is a generalization to all vibrational transitions, the justification of the Markov approximation, and the formula (39) which is not clearly established in [10].

Replacing the sum by an integral,

$$\sum \rightarrow \int d\epsilon \rho(\epsilon) , \quad \rho(\epsilon) |\langle a | \alpha \rangle|^2 \rightarrow \rho_a(\epsilon) ,$$

we obtain

$$D^e(-s) = \left(\frac{\partial \epsilon_a}{\partial \xi}\right)^2 \int_0^{\epsilon_f} d\epsilon_\alpha \int_{\epsilon_f}^{\infty} d\epsilon_\beta \rho_a(\epsilon_\alpha) \rho_a(\epsilon_\beta) \exp[-i(\epsilon_\beta - \epsilon_\alpha)s / \hbar] , \quad (36)$$

where  $\rho_a(\epsilon)$  is the density of states of the orbital  $|a\rangle$ . If we assume that the width of  $\rho_a(\epsilon)$  is on the order of 1eV [23], then  $D^e(-s)$  vanishes for  $s \gg \hbar/1\text{eV} \approx 10^{-15}$  s. During such a short time, the system cannot evolve, and  $D^e(-s)$  may be integrated over  $s$  assuming  $P_n(t-s) \approx P_n(t)$  in (31), which is the Markov approximation. From [10], we have

$$\text{Re} \int_0^t ds \exp(i\omega s) D^e(-s) \approx \pi \hbar^2 \omega \rho_a^2(\epsilon_f) \left(\frac{\partial \epsilon_a}{\partial \xi}\right)^2 .$$

$$\text{Re} \int_0^t ds \exp(-i\omega s) D^e(-s) = 0 \quad . \quad (37)$$

Taking into account the fact that the orbital  $|a\rangle$  is fourfold degenerate [10], we end up with a rate of transition from the vibrational state  $n$  to  $m$  equal to

$$R_{nm}^e = \frac{\pi\hbar}{4\mu} (n \delta_{n,m+1}) \sigma^2 \quad , \quad (38)$$

$$\text{where } \sigma = \frac{\partial \epsilon_a}{\partial \xi} \rho_a(\epsilon_f) \quad .$$

As shown in [10],  $\sigma$  may be determined experimentally. It is the derivative of the number of electrons in the orbital  $|a\rangle$  with respect to the stretching amplitude. Persson assumed that the difference between the dipole moment of the adsorbed ( $D_a$ ) and free ( $D_f$ ) molecule is due to this charge transfer. Then, the effective charge ( $\delta$ ) associated with the stretching of the adsorbed molecule is equal to  $\delta = (\delta^+ + \bar{e}d\sigma)$ , where  $\delta^+$  is the effective charge associated with the stretching of the free molecule,  $\bar{e}$  is the charge of one electron, and  $d$  is the mean distance separating the electron in the orbital  $|a\rangle$  from the metal surface. Using the fact that the transition dipole moment of the free and adsorbed molecule are, respectively,

$$D_f = \delta^+ \left( \frac{\hbar}{2\mu\omega} \right)^{1/2} \quad \text{and} \quad D_a = \delta \left( \frac{\hbar}{2\mu\omega} \right)^{1/2} \quad ,$$

we can estimate  $\sigma$  to be

$$\sigma = \frac{D_a - D_f}{\bar{e}d} \left( \frac{2\mu\omega}{\hbar} \right)^{1/2} \quad . \quad (39)$$

We now compute the part of the memory kernel due to  $H^{rv}$ . Some simple algebra leads to

$$D^r(-s) = \frac{\hbar \delta^2}{2\epsilon_0 U} \sum_k \omega_k \{ \langle p_k^\dagger p_k \rangle \exp(-i\omega_k s) + (\langle p_k^\dagger p_k \rangle + 1) \exp(i\omega_k s) \} . \quad (40)$$

By taking  $U$  large enough, we may replace the sum by an integral

$$\sum_k \rightarrow \frac{U^{1/3}}{2\pi c} \int_0^\infty d\omega_L , \quad \langle p_k^\dagger p_k \rangle \rightarrow n(\omega_L) ,$$

where  $c$  is the speed of light.

We also neglect the term  $(+1)\exp(-i\omega_k s)$ , which gives the damping of the vibrational level due to the vacuum fluctuations of the electric field. Finally, we assume the spectral intensity of the laser to be a Lorentzian centered around  $\omega$ ,

$$n(\omega_L) = N \frac{\Gamma_L}{\pi[\Gamma_L^2 + (\omega - \omega_L)^2]} , \quad (41)$$

where  $\Gamma_L$  is the spectral linewidth of the laser and  $N$  is the density of photons. Because  $n(\omega_L)$  vanishes quickly when  $\omega_L$  is different from  $\omega$ , we may replace  $\omega_k$  in (40) by  $\omega$ . The intensity of the laser is given by:

$$I = \frac{c\epsilon_0}{\delta^2} D^r(0) = \frac{\hbar \omega N}{\pi U^{2/3}} . \quad (42)$$

Finally, we obtain from Eqs. (40)-(42)

$$D^r(-s) = \frac{\hbar \delta^2}{2c\epsilon_0} \int_0^\infty d\omega_L \frac{\Gamma_L [\exp(i\omega_L s) + \exp(-i\omega_L s)]}{\pi[\Gamma_L^2 + (\omega - \omega_L)^2]}$$

or

$$D^r(-s) = \frac{\hbar \delta^2}{2c\epsilon_0} e^{-\Gamma_L s} [\exp(i\omega s) + \exp(-i\omega s)] . \quad (43)$$

The quantity  $D^r(-s)$  does not vanish before  $s$  is larger than  $\Gamma_L^{-1}$ .  $\Gamma_L^{-1}$  is the temporal coherence of the electric field and may be larger than the characteristic time of the evolution of the probabilities  $P_n(t)$ , in which case the Markov approximation is not applicable. Furthermore, we may not then neglect the temporal coherence of the stretching position  $\xi(t)$ . To take this into account, we replace  $\pm\omega$  in (31) by  $\pm\omega + i\Gamma_v$ .  $\Gamma_v^{-1}$  is the temporal coherence of  $\xi(t)$  and is given by

$$\Gamma_v = R_{10}^e = \frac{\pi\hbar\sigma^2}{4\mu} . \quad (44)$$

#### V. Equation of Evolution and Property of the Steady State

By neglecting the integrals

$$\int_0^t ds \exp(\pm i2\omega s) \exp(-\Gamma s) P_n(t-s) ,$$

we can express the kinetic equation (31) in the simple form

$$\dot{\vec{P}}(t) = \frac{\pi\hbar\sigma^2}{4\mu} \vec{D}^> \vec{P}(t) + \frac{\delta^2 I \vec{E}^>}{2\hbar\omega\mu c \epsilon_0} \int_0^t ds \exp(-\Gamma s) \vec{P}(t-s) , \quad (45)$$

where  $\Gamma = \Gamma_L + \Gamma_v$ ,  $\vec{P}(t)$  is the vector  $(P_0(t), P_1(t) \dots)$ ,  $\vec{D}^>$  is the matrix

$$\begin{pmatrix} 0 & 1 & 0 & 0 & 0 \\ 0 & -1 & 2 & 0 & 0 \\ 0 & 0 & -2 & 3 & 0 \\ 0 & 0 & 0 & -n & (n+1) \\ & & & \ddots & \ddots \end{pmatrix} ,$$

and  $\vec{E}^>$  is given by

$$\begin{pmatrix} -1 & 1 & 0 & 0 & 0 \\ 1 & -3 & 2 & 0 & 0 \\ 0 & 2 & -5 & 3 & 0 \\ 0 & 0 & n & -(2n+1) & (n+1) \\ & & & \ddots & \\ & & & & \ddots \end{pmatrix}.$$

In the steady state,  $\dot{P}(t)$  is zero and  $\vec{P}(t-s)$  is equal to  $\vec{P}(t)$ , such that (45) becomes

$$\dot{\vec{P}}(t) = \alpha[\vec{D}^> + \beta\vec{E}^>] \vec{P}(t) = \vec{0} \quad (46)$$

$$\text{with } \alpha = \frac{\pi\hbar\sigma^2}{4\mu} \text{ and } \beta = \frac{2\delta^2 I}{\pi\hbar^2 \omega \Gamma \sigma^2 c \epsilon_0}.$$

In fact, by eliminating " $= \vec{0}$ " on the far right-hand side of Eq. (46), we obtain the kinetic equation within the Markov approximation. In the steady state, the probabilities  $P_n^s$  are given by

$$P_{n+1}^s = [(2v+1)\beta + v] P_n^s - \beta n P_{n-1}^s. \quad (47)$$

This kind of equation admits only one normalized solution [24], given by

$$P_n^s = \left(\frac{\beta}{1+\beta}\right)^n \frac{1}{1+\beta}. \quad (48)$$

The mean number of vibrational quanta is given by

$$\langle n \rangle = \sum_{n=0}^{\infty} n P_n^s = \beta. \quad (49)$$

The power dissipated into the metal is given by the scalar product between  $\alpha\vec{D}^>\vec{P}^s$  and  $(0, \hbar\omega, 2\hbar\omega, \dots)$ , which is equal to

$$\text{Power} = |-\alpha\beta\hbar\omega| = \frac{\delta^2 I}{2\mu c \epsilon_0 \Gamma} \text{ molecule}^{-1}. \quad (50)$$

To know how many times it takes to the system to reach the steady state, we must integrate Eq. (45) numerically. This leads to the iterative equation

$$\begin{aligned}
 P_n(t+\Delta t) = & P_n(t) + \Delta t \cdot \alpha \{ [-nP_n(t) + (n+1)P_{n+1}(t)] \\
 & + \beta \Gamma \int_0^t ds \exp(-\Gamma s) [nP_{n-1}(t-s) + (n+1)P_{n+1}(t-s) \\
 & - (2n+1)P_n(t-s)] \} .
 \end{aligned} \quad (51)$$

To iterate this equation to arbitrary  $t$ , we need not know all the history,  $P_n(t-s)$ , of the system since,

$$\begin{aligned}
 & \int_0^{t+\Delta t} ds \exp(-\Gamma s) P_n(t+\Delta t-s) \\
 & = e^{-\Gamma \Delta t} [\Delta t \cdot P_n(t+\Delta t) + \int_0^t ds \exp(-\Gamma s) P_n(t-s)] .
 \end{aligned} \quad (52)$$

When the anharmonicity of the vibration is high, the laser can only couple the two lowest vibrational levels. The interaction between the molecule and the metal entails a vibrational transition to just the lower level. Then the populations of the levels containing more than one quantum will decay rapidly to zero ( $\alpha^{-1}$  - lifetime). Furthermore, if at  $t = 0$  these levels are not occupied, they will remain empty all the time. In that situation, our problem reduces to a two-level system, and the kinetic equation reduces to

$$\dot{\vec{P}}^a(t) = \alpha \begin{pmatrix} 0 & 1 \\ 0 & -1 \end{pmatrix} \vec{P}^a(t) + \beta \Gamma \begin{pmatrix} -1 & 1 \\ 1 & -1 \end{pmatrix} \int_0^t ds \exp(-\Gamma s) \vec{P}^a(t-s) . \quad (53)$$

Here  $\alpha\beta\Gamma = \Omega^2/2$ , where  $\Omega$  is the Rabi frequency defined by

$$\Omega^2 = \frac{2I}{c\epsilon_0} |\langle 1|M|0 \rangle|^2 / \hbar^2 ,$$

where  $M = \delta\xi$  is the dipole moment operator, and  $\vec{P}^a(t) = (P_0^a(t), P_1^a(t))$ . At the steady state, the population of the upper level and the power dissipated into the metal are given by

$$P_1^a = \frac{\beta}{2\beta + 1} = \frac{\Omega^2}{2\Omega^2 + 2\alpha\Gamma} \quad (54)$$

$$Power^a = \frac{\hbar\omega\alpha\beta}{2\beta + 1} \text{ molecule}^{-1} . \quad (55)$$

These results are formally equivalent to those obtained by van Smaalen, Arnoldus and George (see Section VI of Reference 16), who transformed to dressed states to compute the laser heating of a transparent crystal via adsorbed atoms. They accounted for the detuning,  $\Delta$ , between the frequency of the laser and the vibration, and they neglected the lifetime  $\alpha^{-1}$  and the laser width  $\Gamma_L$ . In any event, by taking the high laser intensity limit, we end up with the same saturation power

$$Power^{a \text{ sat}} = \frac{\hbar\omega\alpha}{2} \text{ molecule}^{-1} . \quad (56)$$

Comparing (54) and (55) to (49) and (50), we observe that the only new feature introduced by the anharmonicity is the saturation factor  $(2\beta + 1)^{-1}$ , so that the effect of the anharmonicity is negligible if  $\beta \ll 1$ .

The kinetic equation (53) can be rewritten in terms of the population inversion as

$$[\dot{P}_1^a(t) - \dot{P}_0^a(t)] = -2\alpha P_1^a(t) - \Omega^2 \int_0^t ds \exp(-\Gamma s) [P_1^a(t-s) - P_0^a(t-s)] . \quad (57)$$

On a time scale shorter than  $\Gamma^{-1}$ , we can describe analytically the behavior of the population inversion. Neglecting the term  $-2\alpha P_1^a$  and estimating  $\exp(-\Gamma s)$  as unity, we can write the solution of (57) as

$$[P_1^a(t) - P_0^a(t)] = -\cos(\Omega t) . \quad (58)$$

Here we have taken the initial conditions to be  $P_0^a(0) = 1$  and  $P_1^a(0) = 0$ . This is the Rabi oscillation, and such behavior cannot be revealed using the Markov approximation. This oscillation will damp on a time scale of  $\Gamma^{-1}$  to reach the steady state defined in (54) and (55).

## VI. Numerical Results

In this section we adopt the numerical data listed in Table I, which correspond to carbon monoxide molecule adsorbed on a copper surface. The laser characteristics correspond to an infrared beam emanating from an optical parametric oscillator pumped by a YAG laser. This beam is focused to obtain a section of  $1 \text{ mm}^2$  and strikes the surface with a small grazing angle of incidence.

From (39) and (46), we obtain [10]

$$\alpha = \Gamma_v = 6.4 \times 10^{11} \text{ s}^{-1} . \quad (59)$$

Since the temporal coherence of the position  $\xi(t)$  ( $\Gamma_v^{-1} = 1.5 \times 10^{-12} \text{ s}$ ) is much smaller than the temporal coherence of the laser electric field ( $\Gamma_L^{-1} > 10^{-11} \text{ s}$ ), we may make the estimation

$$\Gamma = \Gamma_v + \Gamma_L \approx \Gamma_v = \alpha . \quad (60)$$

With this condition, the mean number of vibrational quanta is inversely proportional to the square of  $\alpha$ . This reflects the fact that this number is limited by the rate of damping of the vibrational energy into the metal, as well as by the broadening in energy of the vibrational levels. The broadening decreases the absorption efficiency of the quasi monochromatic laser beam. This does not occur if the linewidth of the laser is greater than the width of the vibrational levels, in which case



$$\Gamma = \Gamma_v + \Gamma_L \approx \Gamma_L . \quad (61)$$

Adopting the numerical data of Table I, and using Eq. (49), we obtain the mean number of vibrational quanta at the steady state to be

$$\langle n \rangle = \beta = 0.03 . \quad (62)$$

The power transmitted from the laser beam to the surface is calculated from Eq. (50) to be

$$\text{Power} = 7 \times 10^{-10} \text{ J s}^{-1} \text{ molecule}^{-1} . \quad (63)$$

From (50) and (60), we observe that the power is inversely proportional to  $\alpha$ , due to the fact that  $\Gamma_L$  is much smaller than  $\Gamma_v$ . If the interaction between the molecule and the substrate is less important, we have a situation where  $\Gamma_L$  is much larger than  $\Gamma_v$ , in which case the power is independent of  $\alpha$ , where  $\alpha$  measures the strength of the interaction between the molecule and the substrate. This holds if the hypothesis of harmonicity remains valid, which means that  $\beta$ , the mean number of vibrational quanta in the steady state, is not too high, say less than 0.1. The region where our model fails depends on the laser characteristics and is given by

$$\log\left(\frac{\alpha}{\Gamma_L}\right) < \log\left(\frac{5\delta^2 I}{\hbar\omega\Gamma_L^2 \mu c \epsilon_0}\right) , \quad (64)$$

where we have assumed  $\alpha \ll \Gamma_L$ . This is illustrated in Fig. 1.

To estimate the time  $\tau$  necessary to reach this steady state, we compute the evolution of the populations of the vibrational levels using (51) and (52). We adopt the initial conditions  $P_n(0) = \delta_{n,0}$ . The evolution of the mean number of vibrational quanta and the occupation probabilities of the

three lowest levels are shown in Figs. 2 and 3 for two different values of  $\beta$ . The populations of the vibrational levels in the steady state for  $\beta$  equal to 1 are presented in Fig. 4, here we take the steady state to be achieved when the mean number of vibrational quanta reaches 90% of its exact value in the steady state.  $\tau$  does not depend noticeably on  $\beta$  and is estimated to be

$$\tau \approx 4\alpha^{-1} \approx 5.6 \times 10^{-12} \text{ s} . \quad (65)$$

This small value indicates that the mean number of vibrational quanta will follow the instantaneous intensity of the laser since the intensity varies on a time scale of the order of  $10^{-9}$  s. In Fig. 5, we show the evolution of the mean number of vibrational quanta both with and without the Markov approximation. We observe that this approximation overestimates the rate of evolution of the system and gives  $\tau$  equal to  $2.3 \alpha^{-1}$ .

## VII. Conclusions

We have derived a simple kinetic equation for the populations of the vibrational levels of a diatomic molecule adsorbed on a metal. The molecule interacts with the electronic degrees of freedom of the metal and an infrared laser beam. This equation can readily be solved and is valid for all laser linewidths, infrared absorption widths of the adsorbed molecule, and time scales. It has been shown that, to compute the evolution of the populations, the Markov approximation is not valid if the temporal coherence of the laser field is greater than the time scale during which the populations are changing. This failure was observed earlier by Beri and George [22].

Our kinetic equation corresponds exactly to the one obtained using the random-phase approximation. The use of this simplification has entailed the neglect of the nondiagonal elements of the density matrix to compute its evolution, and this approximation has remained questionable in the case of the interaction between a laser and a molecule [12]. It has been used extensively, either implicitly in application of the golden rule [14], or explicitly [13,22]. Our theoretical development proves that this approximation leads to the correct kinetic equation for the populations of the vibrational levels. This conclusion should emphasize the validity of some theoretical predictions already given in the literature.

Our results also show the equivalence of the steady-state properties computed using the golden rule [14], the random-phase approximation [12,22], the Markov approximation [13], the transformation to dressed-states technique [15-17], or the Zwanzig projector technique. In the specific situation considered in the previous section, the probability of finding an adsorbed molecule in its first-excited vibrational level is 0.03, which suggests that resonant excitation of a molecule adsorbed on a metal surface could provide a means of laser-enhanced surface reactions.

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Table I: Data used in numerical calculations.Characteristics of the Adsorbate

System considered: CO adsorbed on Cu [3]

$$D_f = 0.1 \text{ Debye}$$

$$D_a = 0.22 \text{ Debye}$$

$$\omega = 2100 \text{ cm}^{-1} \approx 4 \times 10^{14} \text{ s}^{-1} [8]$$

$$d = 7.8 \times 10^{-11} \text{ m} [10]$$

To account for the screening of the electric field by the electronic polarizability of the adsorbed molecule, we adopt  $\delta = 0.6 \text{ \AA}$  [25].

Characteristics of the Laser Beam

$$\text{pulse duration: } 15 \times 10^{-9} \text{ s}$$

$$\text{pulse energy: } 10^{-2} \text{ J}$$

$$\text{beam cross section: } 10^{-6} \text{ m}^2$$

surface enhancement of the intensity by constructive interference between the incident and reflected beam:  $\sim 4$  [20]

$$\text{mea. intensity: } \sim 3 \times 10^{12} \text{ J m}^{-2} \text{ s}^{-1}$$

$$\text{laser width: } \Delta\omega_L < 1 \text{ cm}^{-1} \approx 3 \times 10^{10} \text{ s}^{-1}$$

### Figure Captions

1. Dependence of the power dissipated into the metal on the strength ( $\alpha$ ) of the interaction between the admolecule and the substrate, where

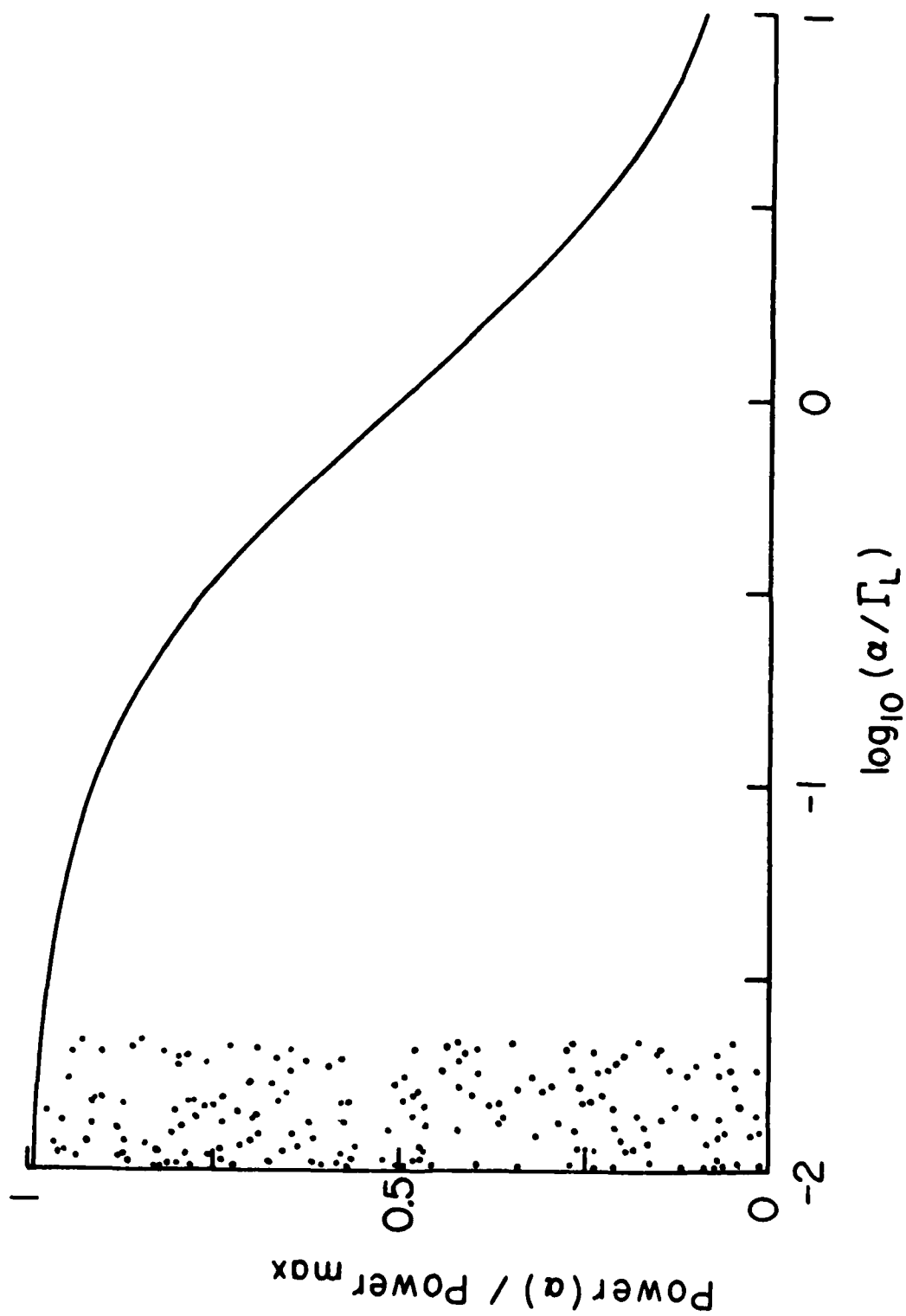
$$\text{Power}_{\max} = \lim_{\alpha \rightarrow 0} \text{Power}(\alpha) = \frac{\delta^2 I}{2\Gamma_L \mu c \epsilon_0} .$$

The region where the hypothesis of harmonicity fails is darkened with points.

2. Evolution of the occupation probabilities of the three lowest vibrational levels,  $P_0(t)$ ,  $P_1(t)$  and  $P_3(t)$ , and of the mean number of vibrational quanta,  $\langle n \rangle$ , for  $\beta = 1$ .
3. Same as Fig. 2, with  $\beta = 0.01$ .
4. Occupation probabilities of the vibrational levels at the steady state for  $\beta = 1$ .
5. Evolution of the mean number of vibrational quanta under the Markov approximation ( $\langle n \rangle_M$ ) and without this approximation ( $\langle n \rangle_{\text{nonM}}$ ) for  $\beta = 0.01$



Fig. 1



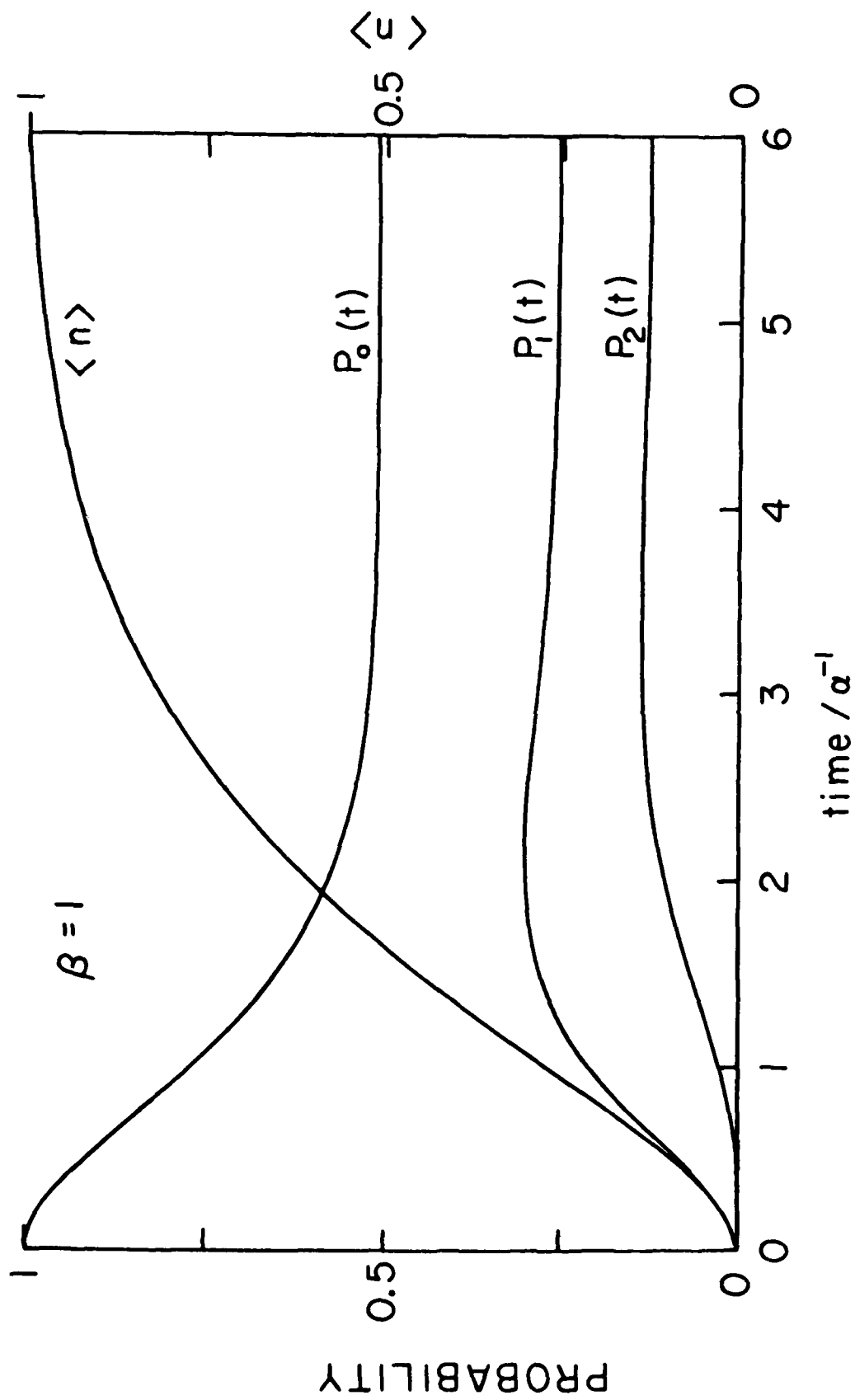


Fig. 2

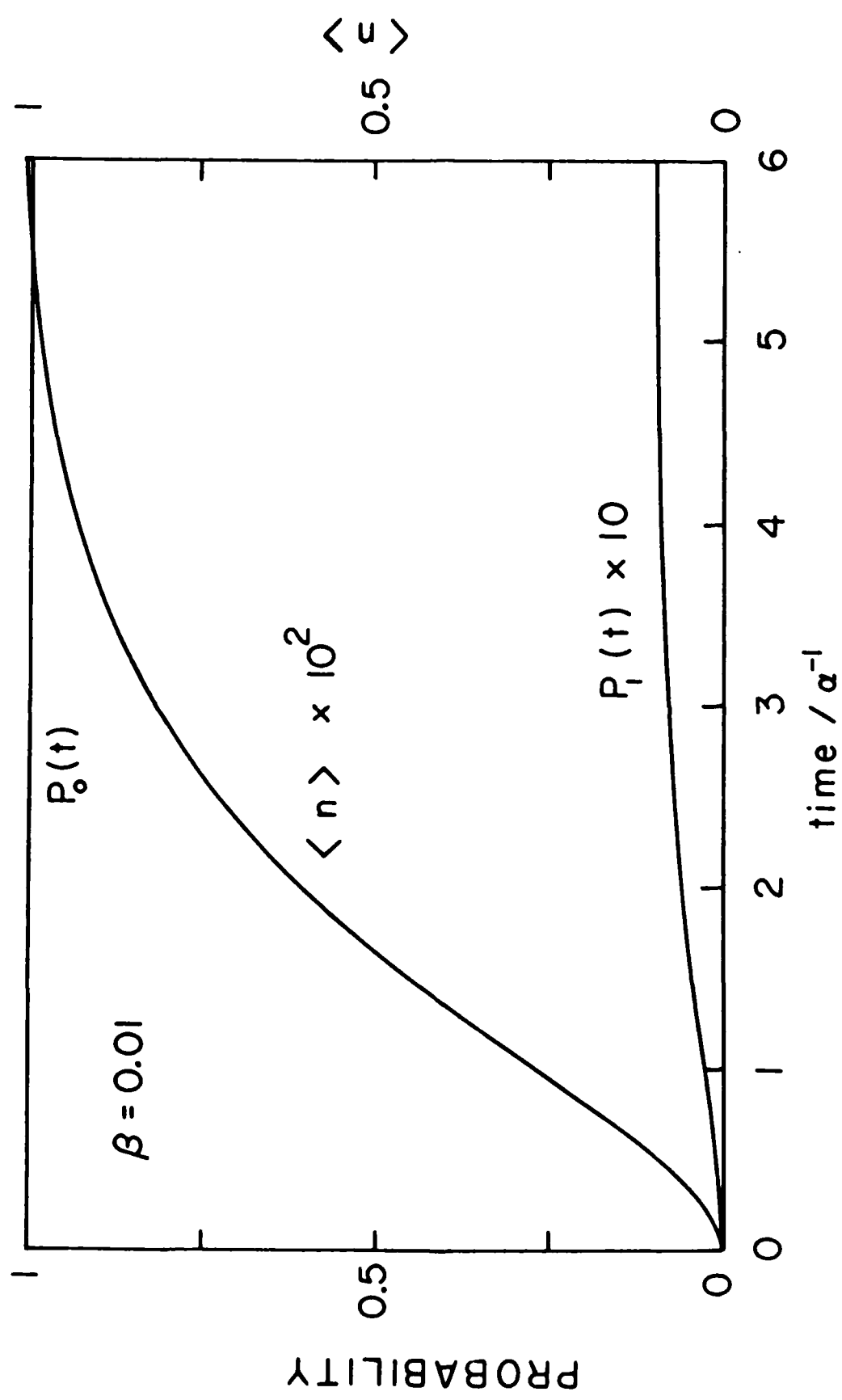


Fig. 3

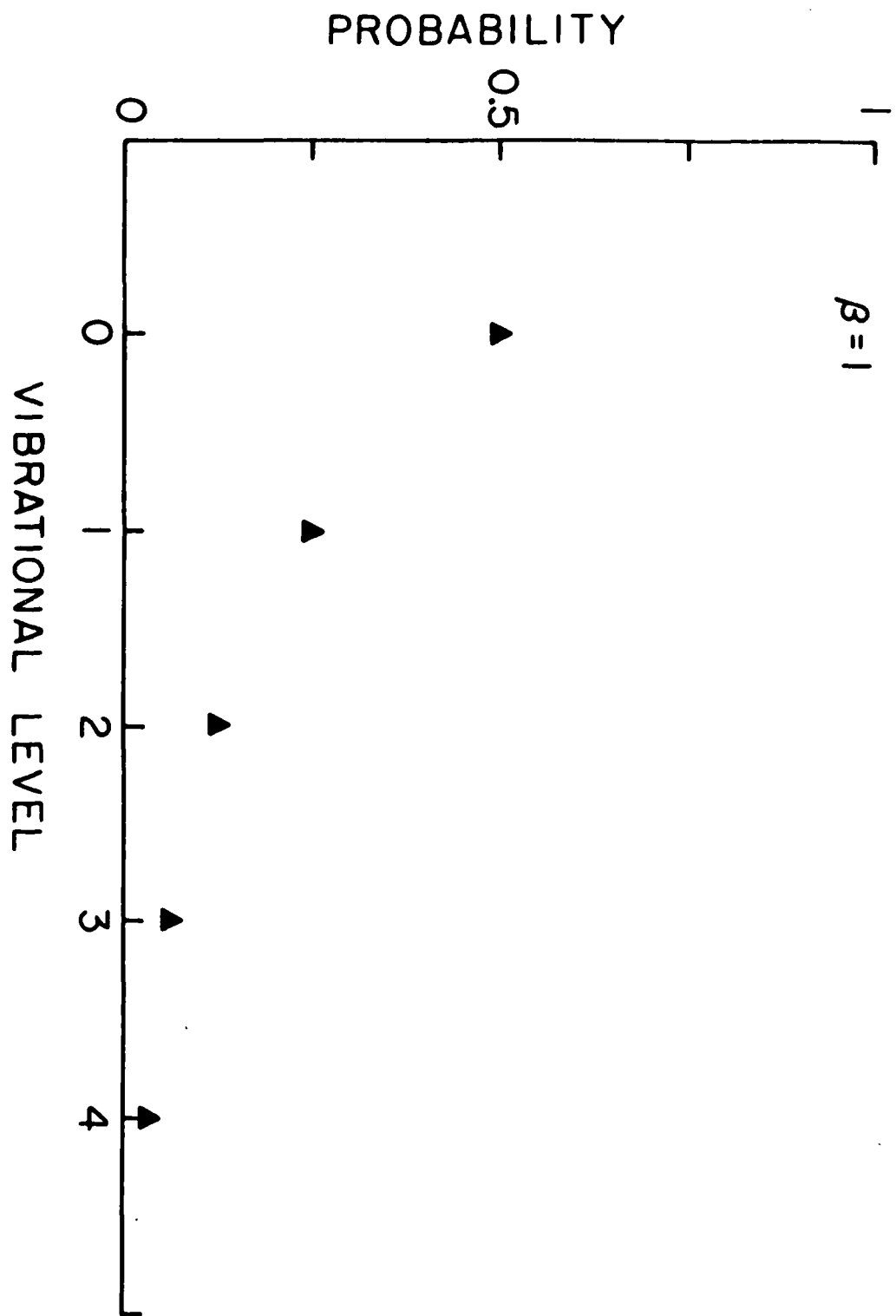


Fig. 4

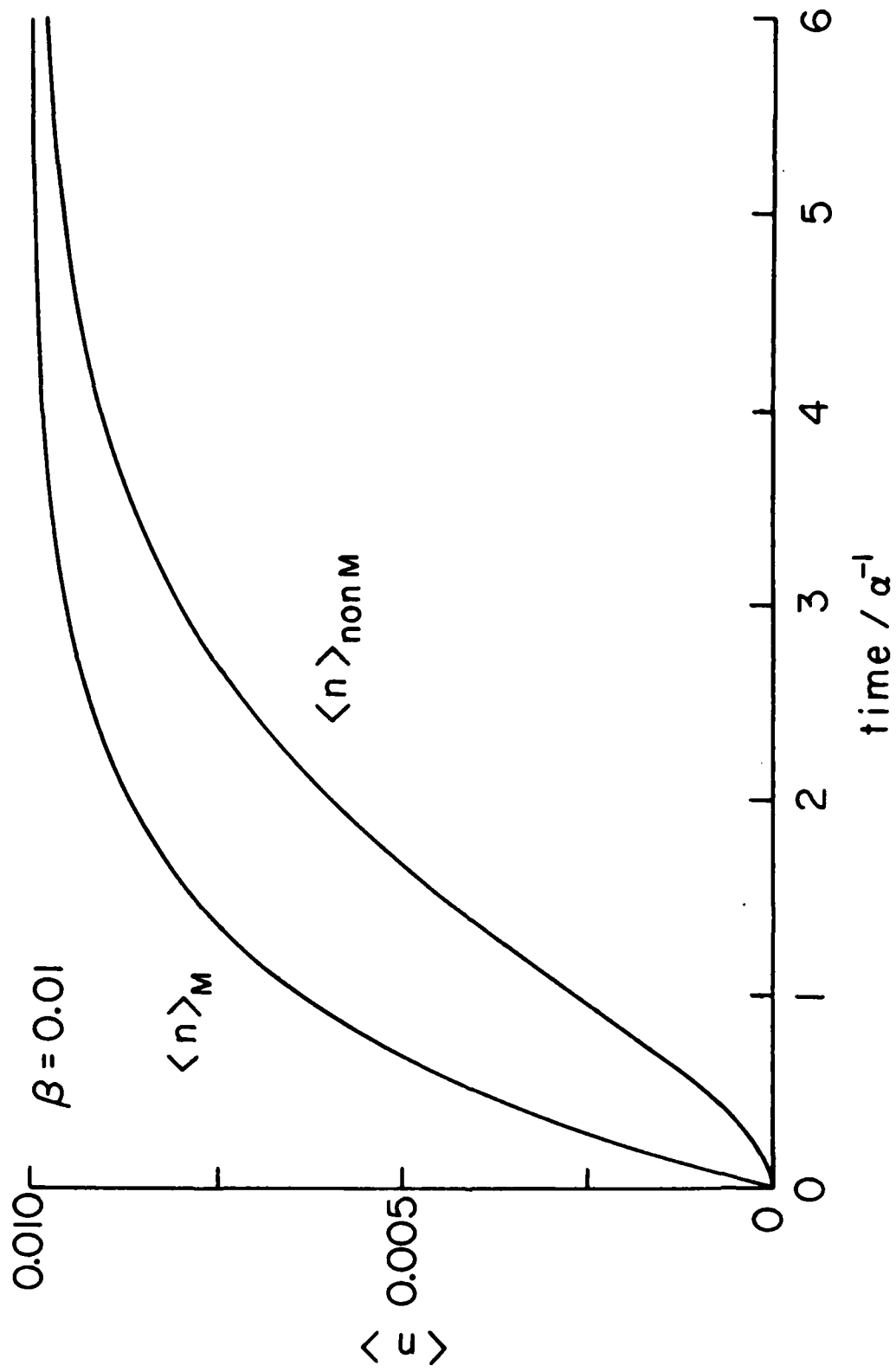


Fig. 5

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ABSTRACTS DISTRIBUTION LIST, 056/625/629

Dr. J. E. Jensen  
Hughes Research Laboratory  
3011 Malibu Canyon Road  
Malibu, California 90265

Dr. J. H. Weaver  
Department of Chemical Engineering  
and Materials Science  
University of Minnesota  
Minneapolis, Minnesota 55455

Dr. A. Reisman  
Microelectronics Center of North Carolina  
Research Triangle Park, North Carolina  
27709

Dr. M. Grunze  
Laboratory for Surface Science and  
Technology  
University of Maine  
Orono, Maine 04469

Dr. J. Butler  
Naval Research Laboratory  
Code 6115  
Washington D.C. 20375-5000

Dr. L. Interante  
Chemistry Department  
Rensselaer Polytechnic Institute  
Troy, New York 12181

Dr. Irvin Heard  
Chemistry and Physics Department  
Lincoln University  
Lincoln University, Pennsylvania 19352

Dr. K.J. Klaubunde  
Department of Chemistry  
Kansas State University  
Manhattan, Kansas 66506

Dr. C. B. Harris  
Department of Chemistry  
University of California  
Berkeley, California 94720

Dr. F. Kutzler  
Department of Chemistry  
Box 5055  
Tennessee Technological University  
Cookeville, Tennessee 38501

Dr. D. DiLella  
Chemistry Department  
George Washington University  
Washington D.C. 20052

Dr. R. Reeves  
Chemistry Department  
Rensselaer Polytechnic Institute  
Troy, New York 12181

Dr. Steven M. George  
Stanford University  
Department of Chemistry  
Stanford, CA 94305

Dr. Mark Johnson  
Yale University  
Department of Chemistry  
New Haven, CT 06511-8118

Dr. W. Knauer  
Hughes Research Laboratory  
3011 Malibu Canyon Road  
Malibu, California 90265

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Dr. G. A. Somorjai  
Department of Chemistry  
University of California  
Berkeley, California 94720

Dr. J. Murday  
Naval Research Laboratory  
Code 6170  
Washington, D.C. 20375-5000

Dr. J. B. Hudson  
Materials Division  
Rensselaer Polytechnic Institute  
Troy, New York 12181

Dr. Theodore E. Madey  
Surface Chemistry Section  
Department of Commerce  
National Bureau of Standards  
Washington, D.C. 20234

Dr. J. E. Demuth  
IBM Corporation  
Thomas J. Watson Research Center  
P.O. Box 218  
Yorktown Heights, New York 10598

Dr. M. G. Lagally  
Department of Metallurgical  
and Mining Engineering  
University of Wisconsin  
Madison, Wisconsin 53706

Dr. R. P. Van Duyne  
Chemistry Department  
Northwestern University  
Evanston, Illinois 60637

Dr. J. M. White  
Department of Chemistry  
University of Texas  
Austin, Texas 78712

Dr. D. E. Harrison  
Department of Physics  
Naval Postgraduate School  
Monterey, California 93940

Dr. R. L. Park  
Director, Center of Materials  
Research  
University of Maryland  
College Park, Maryland 20742

Dr. W. T. Peria  
Electrical Engineering Department  
University of Minnesota  
Minneapolis, Minnesota 55455

Dr. Keith H. Johnson  
Department of Metallurgy and  
Materials Science  
Massachusetts Institute of Technology  
Cambridge, Massachusetts 02139

Dr. S. Sibener  
Department of Chemistry  
James Franck Institute  
5640 Ellis Avenue  
Chicago, Illinois 60637

Dr. Arnold Green  
Quantum Surface Dynamics Branch  
Code 3817  
Naval Weapons Center  
China Lake, California 93555

Dr. A. Wold  
Department of Chemistry  
Brown University  
Providence, Rhode Island 02912

Dr. S. L. Bernasek  
Department of Chemistry  
Princeton University  
Princeton, New Jersey 08544

Dr. W. Kohn  
Department of Physics  
University of California, San Diego  
La Jolla, California 92037



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Washington, D.C. 20375-5000

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Code 6170  
Naval Research Laboratory  
Washington, D.C. 20375-5000

Dr. Dan Pierce  
National Bureau of Standards  
Optical Physics Division  
Washington, D.C. 20234

Dr. R. Stanley Williams  
Department of Chemistry  
University of California  
Los Angeles, California 90024

Dr. R. P. Messmer  
Materials Characterization Lab.  
General Electric Company  
Schenectady, New York 22217

Dr. Robert Gomer  
Department of Chemistry  
James Franck Institute  
5640 Ellis Avenue  
Chicago, Illinois 60637

Dr. Ronald Lee  
R301  
Naval Surface Weapons Center  
White Oak  
Silver Spring, Maryland 20910

Dr. Paul Schoen  
Code 6190  
Naval Research Laboratory  
Washington, D.C. 20375-5000

Dr. John T. Yates  
Department of Chemistry  
University of Pittsburgh  
Pittsburgh, Pennsylvania 15260

Dr. Richard Greene  
Code 5230  
Naval Research Laboratory  
Washington, D.C. 20375-5000

Dr. L. Kesmodel  
Department of Physics  
Indiana University  
Bloomington, Indiana 47403

Dr. K. C. Janda  
University of Pittsburgh  
Chemistry Building  
Pittsburg, PA 15260

Dr. E. A. Irene  
Department of Chemistry  
University of North Carolina  
Chapel Hill, North Carolina 27514

Dr. Adam Heller  
Bell Laboratories  
Murray Hill, New Jersey 07974

Dr. Martin Fleischmann  
Department of Chemistry  
University of Southampton  
Southampton SO9 5NH  
UNITED KINGDOM

Dr. H. Tachikawa  
Chemistry Department  
Jackson State University  
Jackson, Mississippi 39217

Dr. John W. Wilkins  
Cornell University  
Laboratory of Atomic and  
Solid State Physics  
Ithaca, New York 14853

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Department of Physics  
University of California  
Irvine, California 92664

Dr. D. Ramaker  
Chemistry Department  
George Washington University  
Washington, D.C. 20052

Dr. J. C. Hemminger  
Chemistry Department  
University of California  
Irvine, California 92717

Dr. T. F. George  
Chemistry Department  
University of Rochester  
Rochester, New York 14627

Dr. G. Rubloff  
IBM  
Thomas J. Watson Research Center  
P.O. Box 218  
Yorktown Heights, New York 10598

Dr. Horia Metiu  
Chemistry Department  
University of California  
Santa Barbara, California 93106

Dr. W. Goddard  
Department of Chemistry and Chemical  
Engineering  
California Institute of Technology  
Pasadena, California 91125

Dr. P. Hansma  
Department of Physics  
University of California  
Santa Barbara, California 93106

Dr. J. Baldeschwieler  
Department of Chemistry and  
Chemical Engineering  
California Institute of Technology  
Pasadena, California 91125

Dr. J. T. Keiser  
Department of Chemistry  
University of Richmond  
Richmond, Virginia 23173

Dr. R. W. Plummer  
Department of Physics  
University of Pennsylvania  
Philadelphia, Pennsylvania 19104

Dr. E. Yeager  
Department of Chemistry  
Case Western Reserve University  
Cleveland, Ohio 44106

Dr. N. Winograd  
Department of Chemistry  
Pennsylvania State University  
University Park, Pennsylvania 16802

Dr. Roald Hoffmann  
Department of Chemistry  
Cornell University  
Ithaca, New York 14853

Dr. A. Steckl  
Department of Electrical and  
Systems Engineering  
Rensselaer Polytechnic Institute  
Troy, New York 12181

Dr. G.H. Morrison  
Department of Chemistry  
Cornell University  
Ithaca, New York 14853

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